

Quantum transport in DNA wires: Influence of a dissipative environment

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Electronic transport through DNA molecular wires in the presence of a strong dissipative environment is investigated. We show that new electronic states within the bandgap are formed induced by the coupling to the environment. These states show up in the conductance spectrum as a temperature dependent background and lead to a semiconducting to metallic transition with increasing temperature. The transmission at the Fermi level displays a very weak exponential dependence on the wire length as well as activated behavior with increasing temperature. Both results strongly indicate a dominant role of the environment in determining the electronic transport properties of the wire.

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In the emerging field of molecular electronics, DNA oligomers have started in the last decade to attract the attention of both experimentalists and theoreticians [1]. This has been mainly motivated by its exciting potential applications which include its use as templates in molecular devices or by exploiting its self-assembling and self-recognition properties [2]. Alternatively, they might act as molecular wires either in its periodic configuration *e.g.* as poly(GC), or by doping them with metal cations as is the case of M-DNA [3]. As a consequence, the identification of the relevant charge transport channels in DNA systems becomes a crucial issue. Transport experiments in DNA derivatives are however quite controversial [4, 5]. DNA has been characterized as insulating [6], semiconducting [7] or metallic [8, 9]. In particular, Xu *et al.* [9] have recently shown that single poly(GC) oligomers may display metallic behavior when measured in aqueous solution, suggesting the possible role of the environment in enhancing the DC conductivity of DNA. It becomes then apparent that sample preparation and experimental conditions are more critical than in transport experiments on other nanoscale systems. Meanwhile a variety of factors that appreciably control charge propagation along the double helix have been theoretically identified: static [10] and dynamical [11] disorder related to random base pair sequences and structural fluctuations, respectively, as well as environmental effects associated with *e.g.* correlated fluctuations of counterions [12] or with the formation of localized states within the bandgap [4, 13].

In the light of these recent results and inspired by the experiments of Ref. [9], we focus in this letter on the influence of a dissipative environment on the electronic transport in DNA-based molecular wires contacted by electrodes in a two-terminal setup. Surprisingly enough, we find that the interaction of the charge carriers with the environment results in an enhancement of the low-bias conductance with increasing temperature.

Our description basically assumes that only the frontier orbitals of the DNA stack are relevant for charge transport. Frontier orbitals are mainly the highest-occupied

(HOMO) or the lowest-unoccupied (LUMO) molecular orbital. They both have π character and are derived from linear combinations of the p_z orbitals of the base pairs. We thus represent the π (or π^*) orbital stack in a localized orbital picture. The opening of the HOMO-LUMO gap is accounted by a perturbation of the π -stack, along the lines of Ref. [14], in good agreement with first principle calculations [3, 15, 16]. The environment is described by a phonon bath that effectively comprises the influence of counterions and hydration shells, see Fig. 1. In our model an electron injected into the DNA wire can then follow both coherent and incoherent pathways.

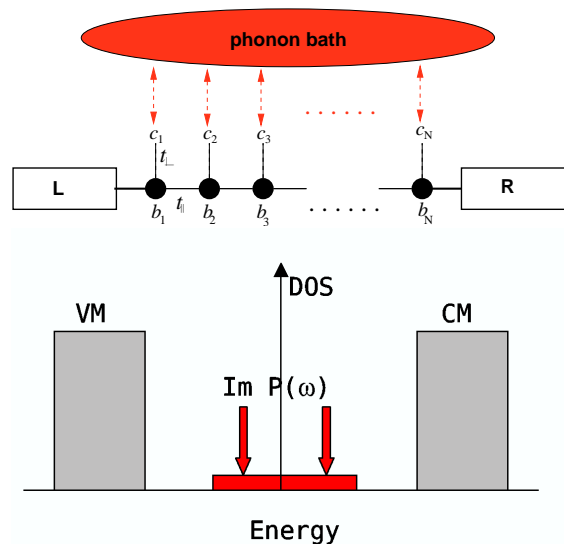


FIG. 1: Schematic representation of the DNA molecular wire in contact with a phonon bath (upper panel) and of the corresponding density of states (lower panel). In the absence of the dissipative bath, valence (VM) and conduction (CM) manifolds are separated by a semiconducting gap. Upon coupling to the environment, a new set of states emerge within the gap. Though strongly suppressed by the dissipative coupling, they contribute with a finite density of states and eventually lead to a conductance enhancement with increasing temperature.

Our main issue is to disclose possible new transport mechanisms induced by a modification of the wire electronic structure in presence of an environment. We especially address the temperature dependence of the electronic gap and the length dependence of the conductance in the strong coupling limit to the bath degrees of freedom. Our results can be summarized as follows. First, a remarkable modification of the transport properties of the wire is found on the low-energy sector of the transmission spectrum. *Bath-induced* states appear in the gap region around the Fermi energy E_F , see Fig. 1 for illustration. They are however strongly washed out due to the strong dissipative effect of the environment, so that they do not manifest as well-defined resonances in the transmission spectrum. Nevertheless, they induce a finite, temperature dependent, density of states within the gap. This leads to a crossover from semiconducting to metallic behavior in the low-voltage regime of the I - V characteristics. Second, a weak exponential length dependence and an activated Arrhenius-like behavior of the transmission at the Fermi energy are found, reflecting the strong contribution of incoherent processes. This behavior can be related to early charge transfer experiments on DNA in solution [8, 17].

We describe the system consisting of a DNA wire containing N base pairs ($\mathcal{H}_C + \mathcal{H}_{C-c}$) [14], contacted to left and right electrodes ($\mathcal{H}_{\text{leads}}$), and in interaction with a phonon bath (\mathcal{H}_B) by the following Hamilton operator:

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_C + \mathcal{H}_{C-c} + \mathcal{H}_{\text{leads}} + \mathcal{H}_B, \\ \mathcal{H}_C &= \epsilon_b \sum_j b_j^\dagger b_j - t_{||} \sum_{\langle i,j \rangle} (b_i^\dagger b_j + \text{H.c.}), \\ \mathcal{H}_{C-c} &= \epsilon \sum_j c_j^\dagger c_j - t_{\perp} \sum_j (b_j^\dagger c_j + \text{H.c.}), \\ \mathcal{H}_{\text{leads}} &= \sum_{\mathbf{k} \in \text{L,R}, \sigma} \epsilon_{\mathbf{k}\sigma} d_{\mathbf{k}\sigma}^\dagger d_{\mathbf{k}\sigma} + \sum_{\mathbf{k} \in \text{L}, \sigma} (V_{\mathbf{k},1} d_{\mathbf{k}\sigma}^\dagger b_1 + \text{H.c.}) \\ &\quad + \sum_{\mathbf{k} \in \text{R}, \sigma} (V_{\mathbf{k},N} d_{\mathbf{k}\sigma}^\dagger b_N + \text{H.c.}), \\ \mathcal{H}_B &= \sum_{\alpha} \Omega_{\alpha} B_{\alpha}^{\dagger} B_{\alpha} + \sum_{\alpha,j} \lambda_{\alpha} c_j^{\dagger} c_j (B_{\alpha} + B_{\alpha}^{\dagger}).\end{aligned}\tag{1}$$

b_j , c_j and $d_{\mathbf{k}\sigma}$ are electronic operators on the central, side chains and the electrodes, respectively, and B_{α} are phonon operators. The onsite energies ϵ_b, ϵ will be set equal to zero, if not stated otherwise. The parameters $t_{||}$ and t_{\perp} describe hopping along the central chain and the coupling between the central chain and the side chain, respectively. The set of bath frequencies Ω_{α} and corresponding coupling constants λ_{α} , $\alpha = 1, \dots, M$, do not need to be further specified. By performing the thermodynamic limit ($M \rightarrow \infty$) later on, the bath can be described by a spectral density $J(\omega) = \sum_{\alpha} \lambda_{\alpha}^2 \delta(\omega - \Omega_{\alpha}) = J_0(\omega/\omega_c)^s e^{-\omega/\omega_c} \Theta(\omega)$, where ω_c is a cut-off frequency and $\Theta(\omega)$ is the Heaviside function [18].

For $\lambda_{\alpha} = 0 \ \forall \alpha$, the model shows a temperature independent gap in the electronic spectrum, the gap being proportional to t_{\perp} (Fig. 1). Valence and conduction manifolds, involving N states each, are symmetric w.r.t. the Fermi level which is the zero of energy (particle-hole symmetry). For nonzero coupling to the bath a more involved behavior may be expected depending on the electron-phonon coupling strength. The interaction with the bath degrees of freedom can be eliminated by performing a Lang-Firsov transformation as given by $\tilde{\mathcal{H}} = e^S \mathcal{H} e^{-S}$ with generator $S = \sum_{\alpha,j} (\lambda_{\alpha}/\Omega_{\alpha}) c_j^{\dagger} c_j (B_{\alpha} - B_{\alpha}^{\dagger})$. Note that only the backbone operators c_j are modified by the above unitary transformation. As a result, the \mathcal{H}_{C-c} Hamiltonian in Eq. (1) is transformed into $(\epsilon - \Delta) \sum_j c_j^{\dagger} c_j - t_{\perp} \sum_j (b_j^{\dagger} c_j \mathcal{X} + \text{H.c.})$ with the operator $\mathcal{X} = \exp[\sum_{\alpha} (\lambda_{\alpha}/\Omega_{\alpha}) (B_{\alpha} - B_{\alpha}^{\dagger})]$, which renormalizes the transversal hopping term and the polaronic shift $\Delta = \sum_{\alpha} \lambda_{\alpha}^2 / \Omega_{\alpha}$.

We focus here on the low-voltage regime in the transport calculations, thus completely neglecting nonequilibrium effects. Even in the presence of incoherent processes, a conductance can be defined as [19]: $g = (2e^2/h) \int dE (-\partial f / \partial E) t(E)$, where $t(E) = 4 \text{Tr} \{ \text{Im} \Sigma_L \mathbf{G} \text{Im} \Sigma_R \mathbf{G}^{\dagger} \}$. Both coherent and incoherent contributions to transport are hidden in the wire matrix Green function \mathbf{G} . In what follows, we always plot the energy dependent transmission function $t(E)$ rather than g to filter out temperature effects arising from the derivative of the Fermi function. For completeness the current as given by $I(V) = (2e/h) \int dE (f(E - eV/2) - f(E + eV/2)) t(E)$ is also shown. The Green function \mathbf{G} can be calculated using equation of motion techniques [20]. One finds:

$$\begin{aligned}\mathbf{G}^{-1}(E) &= E \mathbf{1} - \mathcal{H}_C - \Sigma(E) - t_{\perp}^2 \mathbf{P}(E) \\ P_{\ell j}(E) &= -i \delta_{\ell j} \int_0^{\infty} dt e^{i(E+i0^+)t} e^{-i(\epsilon-\Delta)t} e^{-\Phi(t)}\end{aligned}\tag{2}$$

where $\Sigma(E) = \Sigma_L(E) + \Sigma_R(E)$ and $e^{-\Phi(t)} = \langle \mathcal{X}(t) \mathcal{X}^{\dagger}(0) \rangle_B$ is a dynamical bath correlation function. $\Sigma_{L/R}$ are electrode selfenergies which are calculated in the wide-band limit, *i.e.* $\Sigma_{L,\ell j}(E) = -i \Gamma_L \delta_{1\ell} \delta_{1j}$ and $\Sigma_{R,\ell j}(E) = -i \Gamma_R \delta_{N\ell} \delta_{Nj}$.

We limit our discussion to the strong-coupling limit (SCL) to the bath degrees of freedom, where an appreciable modification of the electronic spectrum is found. Results for the weak coupling case are presented elsewhere [20]. The SCL is defined by the condition $J_0/\omega_c > 1$. Some insight can be gained by approximately performing the integral of Eq. (2). When $J_0/\omega_c > 1$ a short time expansion of the bath correlator $\Phi(t)$ can already give reasonable results. The resulting gaussian integral ($\Phi(t) \sim (\omega_c t)^2$ for $\omega_c t \ll 1$) yields:

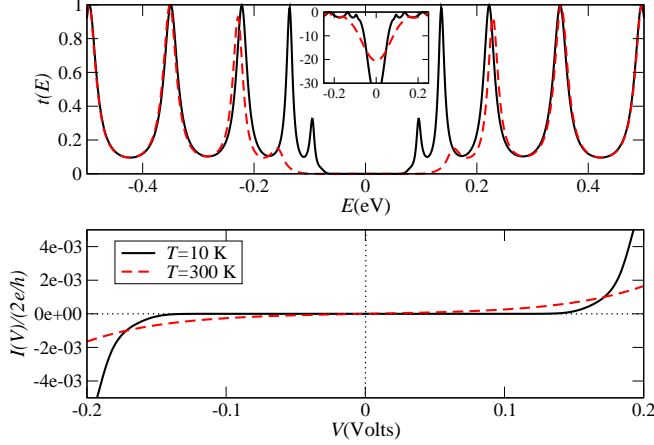


FIG. 2: Upper panel: Transmission $t(E)$ for two different temperatures; the inset is a log-plot of the conductance around $E = 0$ showing the strong temperature dependence of the pseudo-gap. Lower panel: I - V characteristics. Parameters: $N = 15$, $J_0/\omega_c = 2$, $t_{\parallel} = 0.6$ eV, $t_{\perp}/t_{\parallel} = 0.15$, $\Gamma_{L/R}/t_{\parallel} = 0.25$.

$$P_{\ell j}(E) = -i\delta_{\ell j} \frac{\sqrt{\pi}}{2\omega_c\sqrt{\kappa(T)}} \exp\left(-\frac{(E - \epsilon + i0^+)^2}{4\omega_c^2\kappa(T)}\right) \times \left(1 + \operatorname{erf}\left[\frac{i(E - \epsilon + i0^+)}{2\omega_c\sqrt{\kappa(T)}}\right]\right). \quad (3)$$

The temperature dependent function $\kappa(T)$ scales as $\kappa(T) \sim \text{const.}$ and as $\kappa(T) \sim k_B T$ for low and high temperatures, respectively. We note Eq. (3) is independent of the exponent s characterizing the low-frequency behavior of the bath spectral density, $J(\omega) \sim \omega^s$, since the short-time dynamics is mainly affected by the high-frequency bath modes ($\omega > \omega_c$) and the spectral density has a similar asymptotic behavior at high-frequencies for all s .

In Fig. 2 the conductance and the corresponding current are shown. The gap in the transmission spectrum $t(E)$ is seen to increase with temperature and the low-voltage I - V characteristics show a crossover from semiconducting to metallic behavior with increasing temperature. The reason is that in the SCL a *pseudo-gap* rather than a gap in the electronic spectrum is induced by the bath dynamics. An analysis of the real and imaginary parts of $P(E)$, Eq. (3), at low energies helps to understand this. We can show that (i) $\operatorname{Re} P(E) \sim E$ for $E \sim 0$ and (ii) $\operatorname{Im} P(E)$ is peaked at $E = 0$. For comparison, in the absence of the bath $\operatorname{Re} P(E)$ would display a $1/E$ behavior around $E = 0$ [14]. It follows from (i) that additional low energy poles of the wire Green function $\mathbf{G}(E)$ might emerge symmetrically placed around the Fermi energy, building a third electronic manifold. They might show up as resonances in the transmission spectrum inside the gap, see also Fig. 1. We note that they are neither present

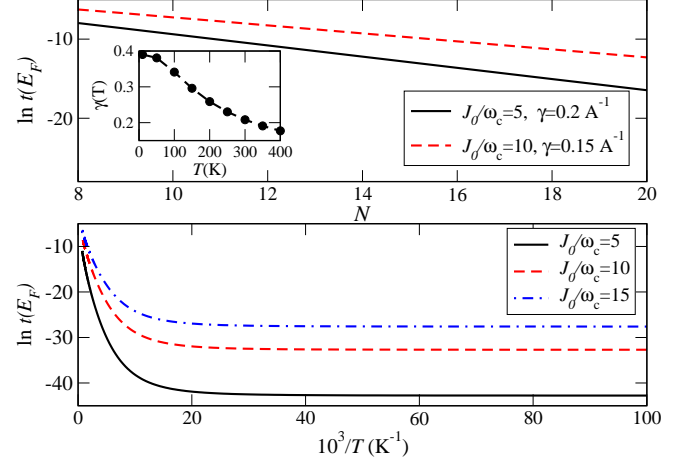


FIG. 3: Upper panel: Length dependence of $t(E_F)$. Parameters: $t_{\perp}/t_{\parallel} = 0.5$, $\Gamma_{L/R}/t_{\parallel} = 0.15$, $T = 300$ K. Inset: temperature dependence of the decay length γ . Lower panel: Arrhenius plot for $t(E_F)$. Parameters: $N = 20$, $t_{\parallel} = 0.2$ eV, $t_{\perp}/t_{\parallel} = 0.4$, $\Gamma_{L/R}/t_{\parallel} = 0.5$.

for $\lambda_{\alpha} = 0$ nor in the weak-coupling limit [20]. For an infinite wire, we would then have three electronic bands. It turns out however that the non-vanishing $\operatorname{Im} P(E)$ has a dramatic influence on these new states. Since they appear in an energy region where $\operatorname{Im} P(E)$ is appreciably different from zero, no well-defined resonances manifest in the low-energy sector of the transmission. Nevertheless, these bath-induced states *do* contribute with a temperature dependent background and eventually lead to an increase in the density of states near $E = 0$ when the temperature grows. Hence, the current may be enhanced at low voltages with increasing temperature.

A controversial issue in transport through DNA-based systems is the actual length dependence of the electron transfer rates or correspondingly, of the linear conductance [17, 21, 22]. Different functional dependences have been found in charge transfer experiments ranging from strong exponential behavior by superexchange mediated electron transfer [21] to algebraic dependences typical of sequential hopping [17, 22]. As far as transport experiments are concerned, Xu *et al.* [9] reported an algebraic length dependence of the conductance for poly(GC) oligomers in solution. Theory has shown that a transition between different regimes may happen as a function of the wire length [23]. We have investigated the length dependence of $t(E_F)$ and found for reasonable parameters an exponential law for energies close to E_F , $t(E_F) \sim \exp(-\gamma L)$, see Fig. 3. At the first sight, this might be not surprising since a gap in the spectrum does exist. Indeed, in the absence of the bath, *i.e.* with an intrinsic semiconducting gap, we get decay lengths γ_{coh} of the order of 2 \AA^{-1} . However, as soon as the interaction with the bath is included, we find values of γ much smaller than expected for virtual tunneling, ranging from

0.15 \AA^{-1} to 0.4 \AA^{-1} . Additionally, γ is strongly dependent on the strength of the electron-bath coupling J_0/ω_c as well as on temperature; γ is reduced when J_0/ω_c or $k_B T$ increases, see Fig. 3, since in both cases the density of states within the pseudo-gap increases. These results clearly indicate that the bath does strongly determine the effective decay length in a way which we can quantify by extracting a γ_{env} term such that $\gamma = \gamma_{\text{coh}} - \gamma_{\text{env}}$. The first contribution γ_{coh} is purely determined by the intrinsic electronic structure of the wire and can be obtained, *e.g.* by means of complex band structure approaches [15, 24]. A γ_{coh} of the order of 1.5 \AA^{-1} has been recently calculated for poly(GC) [15], which compares well with our estimated γ_{coh} . The dependences on J_0 and $k_B T$ are hence contained in the bath-induced contribution γ_{env} .

In Fig. 3, we also show an Arrhenius plot of the transmission at the Fermi energy. Activated behavior can be clearly seen. As expected, the absolute values of the transmission increase with increasing J_0/ω_c . The onset temperature is strongly dependent on the transversal hopping t_{\perp} . The larger t_{\perp} is, the lower the onset temperature is (not shown).

From the length and temperature dependence of $t(E_F)$ the physical picture that emerges is of a charge carrier making an incursion into the side chain and remaining localized there as a result of the strong electron-bath coupling. When the temperature increases, thermal activated hopping to the central chain becomes efficient and the charge carrier can jump back and dissipate into the leads. The temperature at which activated processes begin to occur will thus sensitively depend on the interplay between J_0/ω_c and t_{\perp} .

In conclusion, we have investigated the influence of a dissipative environment on charge transport in a wire model which mimics basic features of the electronic structure of DNA oligomers. We found a strong modification of the low-energy charge transport properties in the strong-coupling regime. Indeed, a *pseudo-gap* is formed and a transition from semiconducting to metallic behavior at low voltages with increasing temperature is found. Alternatively, this may also be seen as a crossover from coherent (low-temperature) to strongly incoherent (high-temperature) transport. We finally mention that the inclusion of a random base pair distribution in the spirit of the Anderson model to account for intrinsic structural fluctuations does not qualitatively change the above picture [20]. Disorder mainly washes out the side bands in the transmission without essentially changing the behavior around the Fermi level. Similarly, shifting the onsite energies on a finite segment of the wire to model the insertion of AT-base pairs in an otherwise homogeneous GC-chain, only leads to a stronger fall-off of $t(E_F)$, without modifying the exponential dependence.

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